

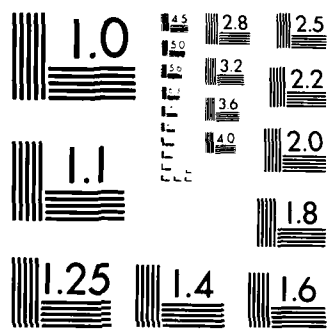
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FLOW REACTOR STUDIES OVER WIDE TEMPERATURE AND PRESSURE RANGES
OF ATOM AND RADICAL REACTION RATES IMPORTANT IN IGNITION AND COMBUSTION

FINAL REPORT

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Reaction rate parameters; flow reactors; O-atom, OH-radical, CH₃O-radical reactions; transition state theory, three-parameter rate constant expressions; radical-radical reactions; ¹⁸O isotope exchange reactions; H + O₂ + M recombination.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The completed research consists of critical evaluations of atom and radical reactions in terms of rate theory, the measurement of elementary reaction rate parameters for several important reactions, and the building and use of a new flow system for the study of the H + O₂ + M → HO₂ + M recombination. The experimental studies include the establishment of the primary products of the O + C₂H₄ reaction, viz. C₂H₃O + H in ~80% yield; the measurement of five H-atom abstraction reactions of OH with C₂H₆ and four Cl- and F-substituted ethanes; the proof, by use of ¹⁸O, that the fast reaction O + HO₂ → OH + O₂ proceeds via an		

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intermediate HO_3 adduct; and the first direct measurement, by laser-induced fluorescence, of the $\text{CH}_3\text{O} + \text{NO}_2$ reaction rate over the temperature range 250 to 473 K. The $^{18}\text{O} + \text{NO}$, O_2 isotope exchange reaction rates were measured and compared with theory, and a new, higher pressure flow reactor apparatus was built and the rate constants for $\text{H} + \text{O}_2 + \text{M}$ measured at 298 K for $\text{M} = \text{He}, \text{N}_2, \text{CH}_4$, and H_2O .

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1. Statement of the Problem Studied

The research carried out under this grant falls into three categories: (a) the critical evaluation of important atom and radical reaction rate constants, their experimental measurement in our and other laboratories, and their understanding in terms of reaction rate theory; (b) the measurement of certain elementary reaction rate parameters for O-atom, OH-radical, and CH₃O-radical reactions in flow reactor (discharge-flow) systems, their comparison with other data, and interpretation in the framework of thermochemical transition state theory; and (c) the design and building of a higher pressure (~100 torr) flow system and the study of the $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ recombination over a wide temperature range.

This work has resulted in a total of nine major publications, three in category (a), five in category (b), and one in category (c). The importance of research of this type cannot be overestimated. It provides the building blocks for all gas phase processes whose complicated overall mechanisms are necessarily composed of individual, elementary steps. Due to advances in computer technology, it has become possible to model these many-step mechanisms if rate information on the elementary steps is available. Beyond supplying this input information, the research also extends our understanding of rate parameters, allows us to predict them with greater accuracy, and provides insight into the fundamental science of the molecular interactions.

2. Summary of the Most Important Results

In an invited paper, "Progress and Prospect in Elementary Reaction

Kinetics/Dynamics of Polyatomics," honoring the 50th anniversary of Eyring and Polanyi's theoretical work on simple gas reactions, the P. I. examined the present state of knowledge of five representative reactions involving four to seven atoms. The brief review of these reaction rate systems showed that excellent progress had been made in experimental measurements as well as in ab initio calculations but that the latter were confined to very simple reactions such as $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$. For more complicated reactions, transition state theory had to be used, and the predictive power was relatively low except for atom transfer steps with well-defined transition states at the top of an energy barrier. In the case of H-atom transfer tunneling effects, the situation has remained unsatisfactory, because depending on the "thinness" of the barrier, i.e. of the imaginary vibration frequency of the reaction coordinate, the tunneling path may account for 90 to 99% of the reaction according to theory, yet the corresponding, strong curvature in Arrhenius diagrams at low temperature has not been reported experimentally.

The second paper under this grant, "Chemical Kinetics and Combustion: Intricate Paths and Simple Steps," was the invited plenary lecture at the 19th International Combustion Symposium in Haifa, Israel, August 1982.

In this paper, the P. I. traced the steps that lead from the overall rate of a combustion process to its detailed mechanism, i.e. sequence of elementary reactions, by way of thermochemistry, sensitivity analysis, and chemical intuition. Ultimately, this sequence leads to the measurement and/or theoretical prediction of the elementary chemical reactions except that the required temperature range is still larger, with upper limits of 1500 to 2000 K. Since it is usually very difficult to do rate measurements at such

high temperatures, it is important to have a large T-base, e.g. 200 to 1000 K from which to do the extrapolation, often with the aid of transition state theory. The close collaboration of modelers, theorists, and experimenters is essential to the success of the overall enterprise.

Whereas the first two papers (above) fall into category (a), the third one, "Primary Products of the $O + C_2H_4$ Reaction," is part of category (b). A major discrepancy between earlier flow reactor and more recent molecular beam results on the primary products of the important $O + C_2H_4$ reaction was resolved.

The major question was whether the principal products were $CH_3 + HCO$ or $C_2H_3O + H$. In our experiments, O and H were measured by vacuum u.v. resonance fluorescence at 130.2 and 121.5 nm, the $O + C_2H_4$ rate constant was measured under condition of excess C_2H_4 , the $H + C_2H_4$ rate constant was measured independently to provide the correction term due to subsequent H-atom loss, and the corrected yield of (H-atoms produced)/(O-atoms reacted) was measured at total pressures of 0.4 to 6 torr. The H-atom yield was found to be $(79 \pm 14)\%$, in reasonable agreement with Y. T. Lee's molecular beam data proving that $C_2H_3O + H$ was the major reaction path.

The fourth paper, "Kinetics of the Reactions of OH with C_2H_6 , CH_3CCl_3 , $CH_2ClCHCl_2$, $CH_2ClCClF_2$, and CH_2FCF_3 ," deals with important combustion initiation processes that were studied by the OH resonance fluorescence technique over temperature ranges from about 250 to 470 K. The data were fitted by two-parameter (Arrhenius) and three-parameter expressions, and the latter were then reduced to Arrhenius expressions centered at 300 K. The Arrhenius A^{300} values were then compared with calculated ones

using Benson-Golden's semiempirical transition state theory. As with our earlier work on CH_4 and nine Cl- and F-substituted methanes, the calculated A-values are in good agreement with experiment on average, but they show large deviations (factors of two to three) in individual cases. This agreement is predicated on a transition state geometry in which the C-H-O bond angle is not 180° but about 150° , and the C-H and H-O partial bonds are extended by 0.3 Å each from their single-bond values. The paper also presents a critical discussion of the use and limitations of three-parameter fits.

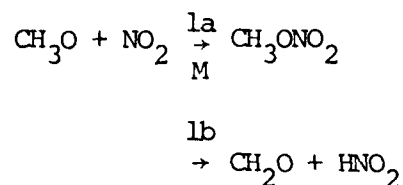
The fifth published paper, "Kinetics of Elementary Radical Reactions in the Gas Phase," an invited Feature Article in the Journal of Physical Chemistry, is the third paper in category (a) under this grant. It describes recent work on radical-molecule and radical-radical reactions as studied by flow reactor or (laser) flash photolysis techniques. Experimental advances are briefly reviewed and several classes of reactions are discussed and compared: "Direct" H-atom abstractions; OH-reactions that proceed via adduct formation; HO_2 -reaction with atoms (H, O, N, Cl, Br) and radicals (OH, HO_2); and radical-molecule reactions that have multiple product channels. The whole field has been invigorated, mostly because of its applications in atmospheric and combustion science. Its greatest needs are (i) closer interaction of experiment and theory; (ii) improved accuracy of rate measurements; and (iii) wide support based on intellectual challenge as well as on societal need.

The sixth paper, "Detailed Course of the $\text{O} + \text{HO}_2$ Reaction," solved, in an elegant way, the question of whether the title reaction was a simple H-atom transfer to produce $\text{OH} + \text{O}_2$, the only exothermic reaction products, or whether the reaction occurred via an

HO_3^+ complex which would spontaneously break down to yield $\text{OH} + \text{O}_2$. Using ^{18}O reactant and examining the OH product by laser-induced fluorescence for the small (0.154 A) isotope shift, we were able to establish clearly that only ^{16}OH was produced, i.e. that the reaction proceeded via HO_3^+ formation. The very fast reaction rate constant of about $5.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ can therefore be interpreted as the high-pressure limit of the $\text{O} + \text{HO}_2 \rightarrow \text{HO}_3^+$ recombination reaction. It is also interesting to note that a seemingly straightforward atom-radical "disproportionation" reaction does not proceed by way of simple atom transfer but by way of a somewhat unexpected intermediate complex.

The seventh paper, "Kinetics of the Reaction of CH_3O with NO_2 ," deals with a reaction that is important in the thermal breakdown of nitrate ester propellants. It was studied at temperatures of 220 to 473 K using laser-induced fluorescence (LIF) detection of CH_3O at 298.5 nm at the downstream end of a flow reactor also equipped with vacuum u.v. detection of atomic species and with chopped molecular beam sampled quadrupole mass spectrometry detection of "dark" species. Reactant radicals or their precursors are generated by IR laser multiphoton dissociation in an upstream cell whose products are swept into the flow tube.

In this case, CH_3 radicals are produced from $\text{C}_6\text{F}_5\text{OCH}_3$ and rapidly converted to CH_3O by reaction with excess NO_2 . The slower $\text{CH}_3\text{O} + \text{NO}_2$ can then be studied under pseudo-first-order conditions with excess NO_2 . At 250 K, the reaction is dominated by the recombination channel, 1a, whereas at 473 K, it is dominated by disproportionation, 1b.



When the data are fitted simultaneously to these channels, a reasonable choice of $k_{1a} = 2.6 \times 10^{-29} (T/300)^{-4.5} \text{ cm}^6 \text{ s}^{-1}$ and $k_{1b} = 9.6 \times 10^{-12} \exp[-1150/T] \text{ cm}^3 \text{ s}^{-1}$ arises, albeit with large uncertainty limits. This represents the first direct study of this reaction and points the way to other, direct measurements of propellant reactions.

The eighth paper, now in press in J. Chem. Phys., "Kinetics of the Isotope Exchange Reaction of ^{18}O with NO and O_2 at 298 K," used the flow reactor, modulated molecular beam mass spectrometer (MMBMS) apparatus to clarify a number of important problems. It must be remembered that if the energy-rich NO_2^{\dagger} or O_3^{\dagger} adducts decompose statistically, the measured isotope exchange rate constant should be one half of the high-pressure-limit $\text{O} + \text{NO} \rightarrow \text{NO}_2^{\dagger}$ and $\text{O} + \text{O}_2 \rightarrow \text{O}_3^{\dagger}$ recombination reaction, and it should also be simply related to the $\text{NO}(v=1) + \text{O} \rightarrow \text{NO}(v=0) + \text{O}$ vibrational relaxation process. In a paper published 21 years ago by Herron and Klein, the $^{18}\text{O} + \text{NO}$ exchange rate constant was reported to be $0.18 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, in strong conflict with experiments and calculations of the high-pressure recombination (~ 3 to 6) $\times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and with the measured $\text{NO}(v=1)$ relaxation by O ($6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$). Our new data showed the exchange rate constant to be much faster, $(3.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and also explained the reason for the earlier, low result. They also suggest that the high-pressure studies had not reached the high-pressure limit which should be $\sim 7.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The agreement with the $\text{NO}(v=1) + \text{O}$ relaxation is excellent.

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